Corrosion mitigation of mild steel in acidic media with the extracts of *Cassia fistula, Bougainvillea spectabilis* leaves and *Mirabilis jalapa* flowers

SYNOPSIS

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Corrosion of metals is a common problem that has an economic as well as environmental impact. Many of the corrosion problems in the industries involve acids namely HCl and H_2SO_4 that are frequently used for acid cleaning, pickling, descaling, acidizing in mining and oil wells. Hence corrosion inhibition in acidic media becomes a necessity. Organic compounds have widely been tried as the corrosion inhibitors for metals and alloys. The corrosion inhibition of mild steel in acidic media in the presence of various organic and inorganic compounds has been reported [Sedhumadhavan et al, (1991), Morretti et al, (1996), Jayaperumal et al, (1997), Bastidas et al, (2000), Larabi et al, (2004), Divakara shetty et al, (2005), Bouklah et al, (2005), Morad, (2007), Khaled, (2008)]. Most of the inhibitors are expensive synthetic chemicals having hazardous property to living creatures and environment. Accordingly these toxic, expensive chemical inhibitors have to be replaced by the inhibitors obtained from natural sources.

The recent research by the electrochemists and corrosion engineers is to find natural organic substances or biodegradable materials to be used as inhibitors. Due to their biodegradability and eco friendliness the trend of using less toxic herbal compounds has come into practice. A number of plant materials have been evaluated for their inhibition efficiency and are reported in the literature [Saleh et al, (1983), Smita verma and Mehta, (1997), Sakthivel et al,(1999), Saratha et al, (2003), Oguzie, (2006), Okafor and Ebenso, (2007), El Etre,(2007), Quraishi et al, (2009), Patel et al, (2009), Eddy and Ebenso, (2010)]

Extracts of naturally occurring products contain mixture of compounds and are biodegradable in nature. Hence the aim of the present study is to explore the performance of acid extracts of *Cassia fistula* and *Bougainvillea spectabilis* leaves and *Mirabilis jalapa* flowers as corrosion inhibitors for mild steel in 1 M HCl and 0.5 M H_2SO_4.

These plants are selected on the basis that these are easily available through out the year, biodegradable and less/non toxic.

The work is presented as five chapters

Chapter 1- Introduction

This chapter gives the definition and chemical process of corrosion, different forms of corrosion, consequences of corrosion, losses due to corrosion, corrosion cost, the importance of corrosion studies, corrosion control methods, Inhibitors- types of inhibitors, metal finishing and pickling, disadvantages and problems due to pickling etc. The chapter briefs the importance of green inhibitors. It details about bioaccumulation. The plant profile of the selected inhibitors is presented.

Objectives

The present research is to replace highly toxic substances with less or non-toxic, environmentally safe materials for corrosion resistance.

- To assess the inhibition efficiency of the selected plant material on the mild steel dissolution in acidic media by Weight loss method and Electrochemical method
- To identify the optimal experimental condition for their maximum inhibition efficiency
- To derive the adsorption kinetics from the weight loss data
- To evaluate the storage stability and durability of the plant extracts
- To study the mechanism of corrosion inhibition by the selected plant extracts
- To assess the environmental safety of the extracts during its use.
- To monitor the effectiveness of the pickling bath for repeated usage in presence of the plant extracts

- ❖ To evaluate the industrial applicability of the selected plant extracts for corrosion resistance

Chapter II – Review of Literature

The study of organic and inorganic compounds as inhibitors for corrosion of metals and alloys specifically mild steel in acidic media are reviewed. Also reviewed the usage of plant materials for corrosion of metals such as Aluminium, Copper, Zinc and Iron and alloys namely stainless steel and mild steel.

Chapter III – Materials and Methods

The composition of mild steel was analysed by using ARL 3460 metal analyzer (Optical emission spectrometer). Preparation of mild steel samples for weight loss studies and Electrochemical measurements and the preparation of the acidic media are discussed.

The inhibiting properties of acid extracts of *Cassia fistula* leaves(CFL), *Bougainvillea spectabilis* leaves(BSL) and *Mirabilis jalapa* flowers(MJF) in 1M HCl and 0.5 M H_2SO_4 are evaluated by Weight loss method (at different concentrations, different temperatures and at various time intervals) and Electrochemical methods namely Potentiostatic polarization and Electrochemical impedance studies. The inhibited metallic surface is examined using FT –IR technique. The durability and the stability of the extracts are studied. Bioaccumulation of these extracts is tested to find out the environmental safety. The bactericidal activity of the acid extracts is tested by agar well plate method using four bacterial stains. All these methods and techniques were explained in this chapter.

The various parameters used in the weight loss method are

Concentration : 0.05, 0.5, 1, 2, 3, 4 and 5% v/v

Temperature : 303, 313, 323, 333 and 343 K

Time period	:	1, 3, 5, 7, 12, 24 and 48 hours
Durability	:	1,2,3 weeks,1,2,3,4,5,6,7and 8 months
Stability	:	2, 4, 6 and 8 months under normal and refrigerated conditions

The instruments used for the study are

Weight measurements	:	Denver 220 D balance
Temperature study	:	Thermostat
Electrochemical study	:	Solartran Electrochemical measurement unit 1284 B
FTIR	:	ARL 3460 metal analyzer
Bioaccumulation	:	Systronics Double beam spectrophotometer 2202

Chapter IV - Results and Discussion

- All the three plant materials (CFL, BSL and MJF) proved as effective inhibitors showing maximum inhibition efficiencies above 90% in both 1M HCl and 0.5 M H_2SO_4 at 5% v/v concentration of the inhibitors. This may be attributed to the increase in surface area covered by the inhibitor molecules with increase in concentration of the inhibitor.
- All the three inhibitors were found to be effective for mild steel corrosion in 1M HCl and 0.5M H_2SO_4 over the studied range of immersion periods and concentrations.
- The efficiency of all the inhibitors increased with increase in immersion period. The optimum immersion period for CFL is12 h in 1M HCl and 3 h in 0.5M H_2SO_4. The maximum efficiency was obtained at 48 h for BSL in 1M HCl and 7 h in 0.5M H_2SO_4. The MJF extract showed a maximum

efficiency at 24 h in 1M HCl and 12 h in 0.5M H_2SO_4. This shows the persistence of the adsorbed inhibitor molecules over a longer period.

- From the studies carried out at different temperatures, the inhibitors were found to be effective at higher temperatures too. There was a regular trend of increase in efficiency with increase in temperature at higher concentrations of the inhibitors. CFL and MJF showed a maximum efficiency at 323 K whereas BSL was effective till 333 K in both 1M HCl and 0.5M H_2SO_4.
- The data from weight loss measurements at different temperatures are fit into different isotherms. The data fitted well for the Langmuir, Freundlich and Temkin isotherms with R^2 values very closer to 1 suggesting that the inhibition is by physical adsorption of the inhibitors on the mild steel surface.
- The higher and positive values of molecular interaction parameter 'a' calculated from the Temkin isotherm shows that there exists an attractive force in the adsorbed layer.
- The number of active sites occupied by the inhibitor molecules was obtained from the slope of El Awady thermodynamic model. The number of active sites ranged from 1 to 3 for all the three inhibitors in Hydrochloric acid as well as in Sulphuric acid medium. This confirms that more than one water molecule is replaced by the phytochemical constituents present in the inhibitors.
- The activation energy E_a and the thermodynamic functions namely the Entropy of adsorption ΔS_{ads}, Enthalpy of adsorption ΔH_{ads}, Free energy of adsorption ΔG_{ads}, heat of adsorption Q_{ads} were calculated from Arrehenius and Erying plots.

- The E_a values were negative and increased in the presence of the inhibitors suggesting the formation of adsorption film of physical nature.
- Enthalpy of adsorption was negative for all the inhibitors in both media which suggests that the adsorption is an exothermic reaction.
- Positive value of entropy is attributed to the spontaneous adsorption of the constituents of the extracts on the mild steel surface. Large positive values of ΔS_{ads} suggest that the rate of adsorption is controlled by activation complex.
- Negative value of Q_{ads} also indicates that the adsorption process is exothermic.
- The negative values of ΔG_{ads} indicate the spontaneous adsorption of the phytochemical constituents of the extracts on the mild steel surface.
- From the polarization curves obtained in the electro chemical study the corrosion potential E_{corr}, corrosion current I_{corr}, Tafel slopes b_a and b_c were noted. Marginal shift in the E_{corr} values and decrease in I_{corr} with the increase in concentration of the inhibitors suggest mixed type of inhibition. Changes in the Tafel slopes b_a and b_c values indicate that the components of the inhibitor influence both anodic dissolution as well as the hydrogen evolution reaction.
- The charge transfer resistance R_{ct} and double layer capacitance C_{dl} were obtained from the Nyquist and Bode plots. The increase in R_{ct} and decrease in C_{dl} values is noted when the concentration of the inhibitor is increased in case of all the three inhibitors in both the acidic media. This is attributed to the formation of a protective adsorption film on the mild steel surface.

- The diameter of the Nyquist plot increased with increase in concentration of the inhibitor which is due to the formation of inhibitive film strengthened by the addition of the inhibitor. Nyquist plots with no loops suggest that the mild steel – inhibitor system is under charge transfer resistance control and the inhibitor is selectively adsorbed on the surface of mild steel.
- The Nyquist plots are not perfect semicircles. The depressed semicircles are due to the presence of pores on the electrode surface or due to the adsorption of the inhibitor on the mild steel surface
- The efficiencies obtained from the weight loss method and electrochemical method when compared showed the same trend of increase in efficiency with increase in concentration of the inhibitors. BSL showed the best efficiency among the three inhibitors studied. The magnitude of the efficiencies obtained by different methods varied. This may be attributed to the fact that Weight loss method gives average corrosion rate whereas Electro chemical methods give instantaneous rates.
- The CFL was reported to contain epicatechin, epiafzelechin, epiafzelechin-3-O-glucoside, procyanidin B2, biflavonoids, triflavonoids, rhein, rhein glucoside, sennoside A, sennoside B, chrysophanol and physcion. BSL was reported to contain D-pinitol, tannins, flavonoids and alkaloids. Reports show that MJF contains betaxanthin, betacyanin and betalains. The phytochemical constituents of these inhibitors mostly comprise of =O, -OH and >NH groups. The interaction of these constituents or the complex formation with the mild steel surface takes place via these active centres.

- Durability of the acid extracts under normal and refrigerated conditions are studied. The study revealed that the inhibitors are stable for six months even when stored under laboratory conditions and hence need not be refrigerated.
- The bioaccumulation of the aqueous extracts was analysed using standard method and all the three inhibitors were found to be environmentally safe.
- All the three extracts were effective under the industrial conditions.

Chapter V – Summary and Conclusion

The summary and conclusion of the present study is discussed in this chapter

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